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Stability and Agglomeration of Alumina Nanoparticles in Ethanol-Water Mixtures

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Abstract

Nanofluids have gained much attention in the last decade due to wide range of engineering applications. Agglomeration among nanoparticles in nanosuspensions accelerates settling of nanoparticles due to gravity and reduces overall thermal conductivity of nanofluid. Settling characteristics of alumina nanoparticles in six different concentrations in different proportions of ethanol and water mixtures are studied. Surfactant free nanofluids are prepared with Alumina nanoparticles of average diameter 40 nm, 50 nm and 100 nm using two-step method. Settling behaviour of nanoparticles in nanosuspensions is observed under natural and sonicated conditions. Photographic technique is used to measure sediment height in a batch sedimentation apparatus. Heights of the sediments are observed for 24 hours with and without sonication at room temperature. It is found that sonication has significant influence on the stability of nanofluids. Effect of ethanol concentration on the sediment ratio is studied with and without sonication. Aggregation among nanoparticles and interaction of particles with fluid mixtures are investigated by performing various analyses such as Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM) and particle size analyser.

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Keywords: nanofluids; sedimentation; agglomeration; sonication; stability

1. Introduction

Dispersion of nanoparticles in liquids in low concentration is termed as nanofluid. Nanofluids have gained much attention due to its distinctive properties in the field of heat transfer, nanocomposite membranes, pigments and drug delivery [1-6]. Settling behavior of nanoparticles in nanosuspensions is a topic of significant interest towards their

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usage in different applications. Limited knowledge is available on the particle-liquid interaction and aggregation among particles. Nanoparticles have high surface area due to smaller in size which increases the Van der Waals attractive forces on the surface of particles. These attractive forces tend to attract other particles to form a cluster known as agglomeration [7]. Formation of agglomerates has negative impact on the stability of nanosuspensions [8-10]. Agglomeration in nanofluids can be reduced by ultrasonication of suspensions. Sonication is the phenomenon when ultrasonic waves pass through different folds of sediment causing disruption among particles. Hence the big agglomerates are broken in to smaller agglomerates.

Alumina is an amphoteric oxide of aluminum which has been used in different investigations for the heat transfer improvement [11]. Rehman et al. [12] investigated the dispersion behavior of alumina nanoparticles in water using different particle loading. They found that sonication has significant effect on the stability of nanofluid. Nanosuspensions with three hours of sonication showed high stability and low agglomeration. Witharana et al. [13] investigated the settling behavior of alumina suspensions (0.5 wt%) at different pH levels. They found that nanosuspensions were stable for 30 minutes at pH 6.3. In another study [14], dispersion behavior of alumina in low (1-5 wt% ethanol) and high (95-100 wt% ethanol) concentrations of ethanol were observed with and without sonication. Dispersed type settling behavior was observed in low concentrations of alumina. Liu et al. [15] studied agglomeration and sedimentation behavior of TiO_2 nanoparticles and reported that nanosuspensions with agglomerate size more than 1000 nm showed poor stability. In a recent study [16], sedimentation behavior of clay, Al_2O_3 and CeO_2 in water, EG and water/EG mixture (50 vol%) was observed using photographic method. It was found that nanosuspensions with low nanoparticle concentration showed better stability than concentrated nanosuspensions. Manjula et al. [17] investigated dispersion behavior of alumina nanoparticles in water and reported the effect of pH and stabilizer on the sediment heights of the nanosuspension. They found that stability of nanosuspensions can be improved by optimizing pH level and addition of stabilizer. In our previous work [18], dispersion behavior of ZnO nanoparticles in ethanol-water mixture was studies at different concentrations with and without sonication. It was observed that stability of the nanofluids can be improved using ultrasonication.

The objective of presented work is to study the effect of sonication on the dispersion behavior of alumina nanoparticles in ethanol-water mixtures. Settling behavior of nanoparticles in different proportions of ethanol and water are presented under natural and sonicated conditions. Stability of alumina based nanofluids is observed using sedimentation technique. Particle-liquid interaction and agglomeration has been studied using Fourier transform infrared spectroscopy (FTIR) and transmission electron microscopy (TEM), respectively. It is evident from many investigations [19-21] that sonication has significant effect towards the improvement in stability of nanosuspensions.

Nomenclature

SR	sediment ratio
H_S	sediment height
H_T	total height of sediment

2. Methodology

Alumina nanoparticles of average particle sizes 40 nm (≥ 99.5%, MK Nano), 50 nm (99.9%, SS Nano) and 100 nm (99.9%, MK Nano) are used to prepare nanofluids. Nanoparticles with six different concentrations (0.1, 0.3, 0.5, 1, 3, 5 wt%) are added in different proportions of ethanol concentrations (0-100 wt%) using Two step method. The nanosuspension samples are prepared in flat bottom glass test tubes (16 x 125 mm). Batch sedimentation apparatus is used to observe the settling characteristics of nanofluids using visualization technique at room temperature. FTIR analysis (Perkin-Elmer) has been performed to study interaction of nanoparticles with mixture of liquids. Agglomeration effect has been observed by using TEM images (Zeiss, 200 kV) for sonicated and without sonicated samples. Average agglomerate size is determined using particle size analyzer (Malvern Zetasizer Nano s90) for non-sonicated samples.

To study the natural settling behavior, the nanosuspensions are allowed to settle down under gravity and sediment heights are measured with respect to time for 24 hours. The nanofluid samples are then sonicated for 12 hours using an ultrasonic agitator (Transsonic, 40 kHz). The sediment ratio for sonicated samples are observed for 24 hours and compared with non-sonicated samples. Surfactant free nanosuspensions are prepared without adjusting pH values to study natural settling behavior of alumina nanoparticles. Sediment ratio (SR) has been calculated in terms of sediment height and total height of sample, given in equation (1).

$$SR = \frac{H_S}{H_T} \tag{1}$$

3. Results and discussion

3.1. Particle liquid interaction

FTIR spectroscopy is performed to study the interaction between particles and liquids. Functional groups of C-O, C-H and O-H are confirmed and minor peak shifts are observed in the mixture of ethanol and water shown in Fig. 1 (a). FTIR spectra for Al_2O_3 (40 nm), Al_2O_3 (50 nm) and Al_2O_3 (100 nm) are shown in Fig. 1 (b), (c) and (d), respectively. Al-O-Al bending vibration is detected at 1128.03 cm^{-1}, 1122.41 cm^{-1}, 1191.34 cm^{-1} in alumina nano-powders of sizes 40 nm, 50 nm and 100 nm, respectively. Similar trend was observed in previous literature [22]. Minor peak shifts are observed when the nano-powders are mixed with liquid. The absorption peaks of Al-O-Al are shifted to 1047.31 cm^{-1}, 1045.02 cm^{-1} and 1083.09 cm^{-1} in nanofluids for Al_2O_3 40, 50 and 100 nm respectively. Detection of O-H group in the nano-powders can be attributed to the presence of moisture content. New functional groups are not detected in nanofluids. This confirms that there is no reaction between nanoparticles and base fluids.

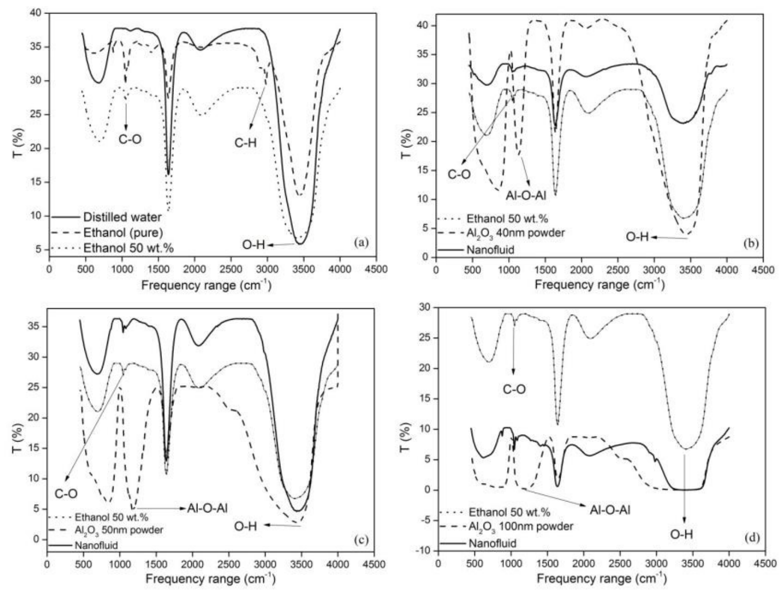

Fig. 1. FTIR spectra of (a) Distilled water, Ethanol and Ethanol-water (50 wt%); (b) Ethanol-water (50 wt%), Al_2O_3 (40 nm) powder and Al_2O_3 (40 nm)/Ethanol-water (50 wt%) nanofluid; (c) Ethanol-water (50 wt%), Al_2O_3 (50 nm) powder and Al_2O_3 (50 nm)/Ethanol-water (50 wt%) nanofluid (d) Ethanol-water (50 wt%), Al_2O_3 (100 nm) powder and Al_2O_3 (100 nm)/Ethanol-water (50 wt%) nanofluid.

3.2. Agglomeration in nanosuspensions

Agglomeration of alumina nanoparticles in ethanol-water mixtures are investigated using particle size analyzer. It is found that aggregation takes place when alumina particles are added into ethanol-water mixtures. The agglomerate size is reached up to micron level for all types of nanoparticles under investigation. Size distribution of alumina nanoparticles in ethanol water mixture is shown in Fig. 2. The analysis shows that average particle/agglomerate size for Al_2O_3 40, 50 and 100 nm is increased to 2152 nm, 2809 nm and 2065 nm, respectively, at scattering angle 173^o. Transmission electron microscopy is used to confirm the agglomeration of nanoparticles and to observe the effect of sonication. TEM images are taken with and without sonication at 50 kX, shown in Fig. 3. It is observed that sonication has significant effect on the stability of alumina suspensions. It is evident from the TEM images that big agglomerates are broken down into smaller agglomerates after sonication.

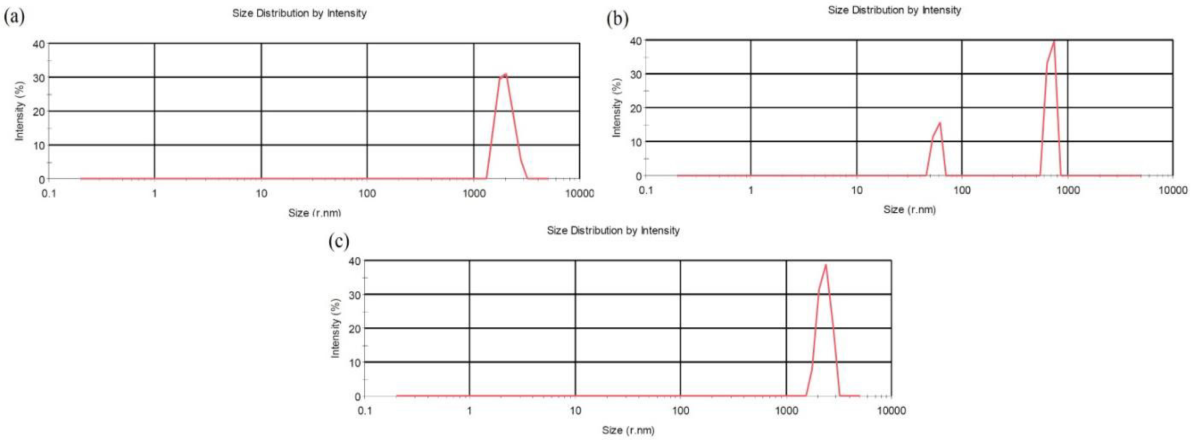

Fig. 2. Particle size distribution by intensity for non-sonicated samples of (a) 0.3 wt% Al_2O_3 (40 nm) dispersed in ethanol-water (50 wt%); (b) 0.3 wt% Al_2O_3 (50 nm) dispersed in ethanol-water (50 wt%); (c) 0.3 wt% Al_2O_3 (100 nm) dispersed in ethanol-water (50 wt%).

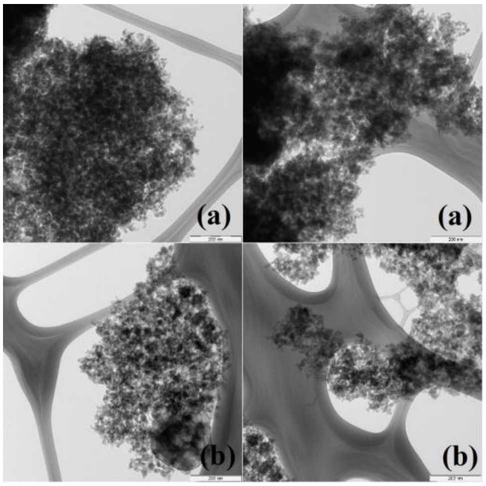

Fig. 3. TEM images for Al_2O_3 (40 nm) dispersed in ethanol-water mixture (50 wt%) (a) without sonication; (b) with sonication (12 hours).

3.3. Effect of concentration of nanoparticles

3. 3. 1 At low concentrations of alumina

Nanosuspensions are prepared at different concentrations (0.1, 0.3 and 0.5 wt%) of alumina nanoparticles to observe the dispersion behavior of nanofluids at low particle loading. Dispersed type settling is observed in all samples of nanofluids. Sediment height is observed to be increased from bottom in all samples of nanofluids with low concentrations of alumina. Settling behavior of 0.5 wt% Al_2O_3 (100 nm) in ethanol-water mixtures (0-50 wt%) without sonication is shown in Fig. 4. All samples of nanosuspensions settle down within 8 hours except pure ethanol. It is observed that alumina nanoparticles in pure ethanol show better stability than all other nanosuspensions.

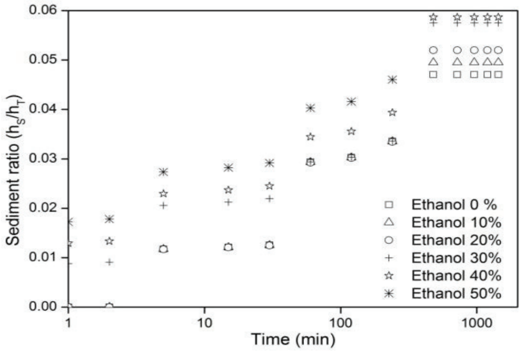

Fig. 4. Settling behavior of 0.5 wt% Al_2O_3 (100 nm) in ethanol-water mixtures (0-50 wt%) without sonication.

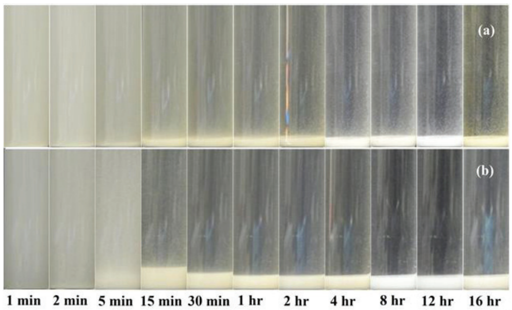

Fig. 5. Settling behavior of 0.5 wt% Al_2O_3 (100 nm) dispersed in ethanol-water mixture (10 wt%) (a) without sonication; (b) with sonication.

The nanosuspensions are sonicated using ultrasonic bath agitator for 12 hours. It is observed that stability is improved for all nanofluid samples after sonication. No sediment is obtained in pure ethanol samples for 24 hours. Nanosuspensions with 0.1 and 0.3 wt% alumina in different proportions of ethanol exhibit no sediment for first 30 min after undergoing ultrasonication. It is observed that sediment behavior of nanofluids of 0.5 wt% alumina turned to flocculated type sedimentation after treating with sonication. Photographic comparison of settling behavior of 0.5 wt% Al_2O_3 dispersed in ethanol-water mixture (10 wt%) with and without sonication is shown in Fig. 5.

3. 3. 2 At high concentrations of alumina

Nanosuspensions are prepared with 1, 3 and 5 wt% of alumina in different proportions of ethanol-water mixtures to study the settling behavior in high concentrations of nanoparticles. Flocculated type sedimentation is observed in all nanofluid samples except nanosuspensions with pure ethanol. Pure ethanol based nanofluids shows dispersed type behavior and better stability as compared to other nanofluid samples. Settling heights in nanosuspensions with 1 wt% alumina is observed to be constant with respect to time which may be the critical alumina concentration in nanosuspensions. The sediment behavior turned to flocculated type after sonication shown in Fig. 6 (a). Fig. 6 (b) represents the settling behavior of 3 wt% alumina with and without sonication in ethanol-water mixture. It is observed that sediment height in nanofluids is increased after treating with sonication. Nanoparticles tend to remain suspended in ethanol-water mixtures for longer time after ultrasonication. Photographic comparison of 5 wt% Alumina (50 nm) in ethanol-water mixture (50 wt%) is shown in Fig. 7.

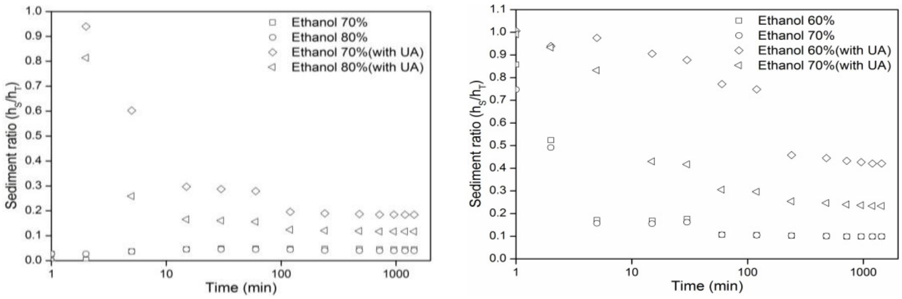

Fig. 6. (a) Sedimentation behavior of 1 wt% alumina (40 nm) in ethanol-water mixtures (70 wt% and 80 wt%) with and without sonication; (b) Settling behavior of 3 wt% Al_2O_3 (40 nm) in ethanol-water mixture (60 wt% and 70 wt%) with and without ultrasonic agitation (UA).

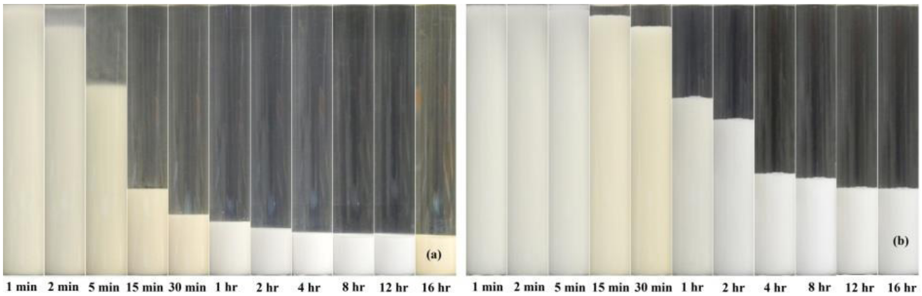

Fig. 7. Photographic comparison of dispersion behavior of 5 wt% alumina (50 nm) in ethanol-water (50 wt%) (a) with sonication; (b) without sonication

3.4. Effect of ethanol-water proportions

Base fluid properties have significant effect on the dispersion behavior and stability of nanofluids. Viscosity of ethanol-water mixtures are higher than the pure liquids which peaks at 50 % ethanol [23, 24]. It is observed that sediment heights of nanosuspensions are following the same pattern as viscosity of the base fluids. It is evident from the photographic comparison of sediment heights at different proportions of ethanol-water mixtures, shown in Fig. 8. Pure ethanol based nanofluids exhibits different settling behavior than all other samples and the particles tend to remain suspended for several days. It is found that high alumina concentrations in pure ethanol exhibits mixed type sedimentation after treating with sonication [14]. Pictures are taken after 30 days and it is found that settling velocity of nanoparticles in suspension is much lower than other solid-liquid mixtures, shown in Fig. 9.

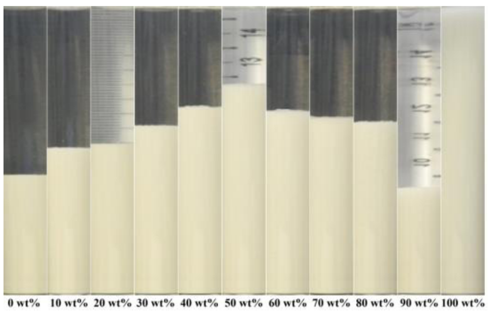

Fig. 8. Photographic comparison of settling characteristics of 5 wt% Al_2O_3 40 nm (after sonication) in different proportions of ethanol-water (0-100 wt%) after 1 hr.

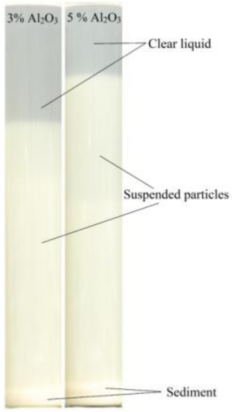

Fig. 9. Settling behavior of Alumina (100 nm) after 30 days in pure ethanol.

4. Conclusion

Recent progress in the field of nanotechnology, especially nanofluids, has provided evolution in the variety of engineering applications such as heat transfer intensification, nano-coatings, medicines and nanocomposite membranes. Stability of nanoparticles in liquids is one of the key factors towards efficient exploitation of smart fluids. Knowledge of dispersion behavior of nanoparticles in different combination of liquids is limited and there is need to explore novel nanofluids with improved properties. Dispersion behavior of alumina in the binary mixture of ethanol and water is studied at low and high particle loading. It is observed that agglomeration has negative impact on the stability of nanofluids. Agglomerate sizes can reach up to micron level which fastens the sedimentation process. It is observed that sonication can improve the stability of nanofluids. Nanofluids with low concentration of nanoparticles exhibits dispersed type settling behavior while high concentration of nanoparticle shows flocculated type sedimentation. It is observed that pure ethanol based nanofluids are well stable than other samples and exhibits mixed type settling behavior. The study can be a gateway of introducing and stabilize metallic nanoparticles in ethanol-water mixtures to achieve high thermal properties of fluid.

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